

Interaction effects in transport through molecular monolayers

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We theoretically investigate the effect of inter-molecular Coulomb interactions on transport through molecular monolayers (or other devices based on a large number of nanoscale conductors connected in parallel). Due to the interactions, the current through different molecules become correlated, resulting in distinct features in the non-linear current-voltage characteristics, as we show by deriving and solving a type of modified master equation, suitable for describing transport through an infinite number of interacting conductors. Furthermore, if some of the molecules fail to bond to both electrodes, charge traps can be induced at high voltages and block transport through neighboring molecules, resulting in negative differential resistance.

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Introduction. It is well known that when N macroscopic resistors, each with a conductance G , are connected in parallel, the total conductance is given by $G_T = NG$. However, this is no longer true if the currents flowing through the individual resistors are correlated, i.e., if the current through one resistor is affected by the current through its neighbors, e.g., due to Coulomb interaction between charge carriers. Such correlation effects can be expected to be important in nanoscale systems, where the conductors are very close to each other and where, because of the quantized nature of the electron charge, current flow can be associated with significant fluctuations of the charge on the resistors.

One interesting example is molecular electronic devices based on a self-assembled molecular monolayer, sandwiched between metallic electrodes [1–3]. Compared with single-molecule junctions, monolayer devices offer better reproducibility and stability, and the larger currents are easier to measure. They have been used to investigate a number of interesting molecular transport effects, such as negative differential resistance (NDR) [4], switching [5], and spin-selective tunneling [6, 7]. Although the experiments are usually interpreted within a single-molecule picture, direct experimental comparisons between monolayer and single-molecule junctions [8] have found large differences, i.e., $G_T \neq NG$. Such differences have been discussed in terms of static changes to the local molecular environment in a monolayer device, e.g., due to rearrangement of molecular or surface charges, or interactions between constant molecular dipole moments [9–11].

In this work, we investigate the *dynamic* transport effect resulting from Coulomb interactions between charges being transported through neighboring molecules in a monolayer. The inter-molecular Coulomb interactions not only lower the conductance ($G_T < NG$), but qualitatively change the non-linear current-voltage characteristics of the device, as we show by deriving a type of modified master equation for the nonequilibrium current, as well as the voltage-dependent charging of the monolayer. If the source and drain tunnel couplings dif-

fer, the inter-molecular Coulomb interactions give rise to a voltage-asymmetric current-voltage characteristic, $I(V) \neq -I(-V)$, the shape of which provides an experimental fingerprint of the interactions. Furthermore, if some molecules form bonds only with one electrode, we show that NDR can occur, since charge traps are formed within the layer and, through the inter-molecular Coulomb interaction, block transport through neighboring molecules. Knowledge of the generic transport signatures of inter-molecular Coulomb interactions, derived in the present work, should be very helpful when interpreting data from molecular monolayer devices and trying to separate the genuinely single-molecule transport effects. For simplicity, we use terminology like "molecule" and "monolayer", but the results are of much more general importance, and apply, for example, to transport through many quantum dots connected in parallel, carbon nanotubes bundled together in a rope, or arrays of nanoparticles, just to give a few examples. The new type of master equation we develop, which describes the correlated non-equilibrium charge distribution among interacting conductors, should form a useful starting point also for studies of a wider range of interacting mesoscopic systems.

There has been a significant amount of prior work investigating the transport effects of an inter-molecular tunnel coupling, see e.g., Refs. 12–15. However, in contrast to Coulomb interactions, tunnel couplings decay exponentially with the molecular separation. Several works have also studied transport through two parallel-coupled quantum dots [16–18], including the effects of inter-dot Coulomb interactions.

Basic physical picture and model. Figure 1 shows a sketch of a molecular monolayer between metallic source and drain electrodes. In Fig. 1(b), we focus on two molecules within the layer and illustrate the basic transport effect of inter-molecular Coulomb interactions, and indicate the molecular transmission resonances (the vertical direction therefore indicates a direction both in real space and in energy space). When an electron tunnels

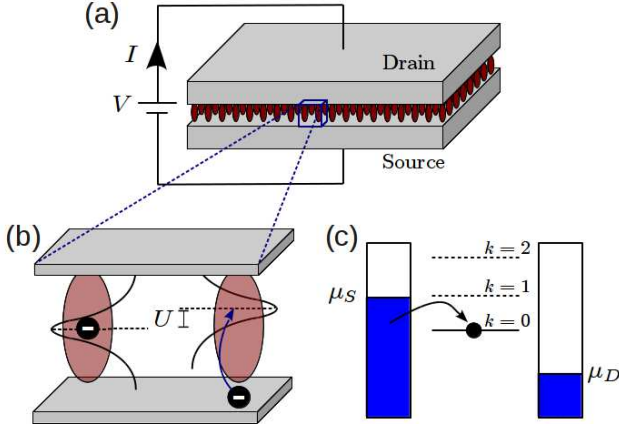


FIG. 1. (Color online). (a) Sketch of the molecular monolayer device. (b) Zoom in on two of the molecules in the upper panel, together with an energy-space representation of the molecular transmission resonances. Due to the intermolecular Coulomb interaction, the resonance seen by an electron tunneling into a molecule is shifted by U if one of its neighbors is charged. (c) Level diagram showing tunneling into the LUMO of a single molecule. The LUMO is shifted by kU when k neighboring molecules are occupied (higher-lying dashed lines).

into a molecule, it experiences the electric field from charges localized on neighboring molecules, which leads to a shift of the effective transport resonance. Therefore, when the bias voltage, V , is just barely large enough to allow resonant transport through a molecular orbital (the HOMO or LUMO is inside the bias window), transport can still be suppressed if neighboring molecules are charged. In the limit of weak tunnel coupling, where transport is dominated by single-electron tunneling, and at low temperatures, we therefore expect a single molecular orbital to give rise to multiple transport resonances: One when the bias is large enough to allow tunneling into the LUMO or out of the HOMO, and additional ones when this becomes possible also when $k = 1, 2, \dots$ neighboring molecules are charged, see also Fig. 1(c). This is in contrast to the result without inter-molecular interactions, where only a single resonance occurs. Below we calculate the detailed current-voltage curves for different interaction strengths.

The distance between molecules in a monolayer depends on the molecular species and contact materials, but is typically $d \sim 1$ nm in a dense monolayer. A rough estimate gives the interaction between electrons on neighboring molecules as $U \sim e^2/(4\pi d\epsilon_0\epsilon_r) \sim 1$ eV/ ϵ_r . The relative permittivity, ϵ_r , within the monolayer may be rather large and the interaction strength further decreased by screening from conduction electrons in the electrodes [19]. However, a U of the same order of magnitude as the thermal energy at room temperature still seems reasonable. In other mesoscopic systems, U is likely much smaller ($U = 0.15 - 0.4$ meV between strands

of nanotubes within a nanotube rope was found in recent experiments [20, 21]), but can still dominate the transport physics at low temperatures.

To focus on the interaction effects, we study the simplest possible molecular model, including only a single spin-less orbital (chosen as the LUMO for definiteness). The Hamiltonian of the monolayer device is $H = \sum_i (H_{ML}^i + H_T^i) + H_{res}$, where

$$H_{ML}^i = \epsilon_i n_i + \frac{1}{2} \sum_j U_{ij} n_i n_j, \quad (1)$$

$$H_{res} = \sum_{pr} \epsilon_{pr} n_{pr}, \quad (2)$$

$$H_T^i = \sum_{pr} t_{ri} c_{pr}^\dagger d_i + h.c.. \quad (3)$$

Here, ϵ_i is the energy of the LUMO of molecule i , which has occupation $n_i = d_i^\dagger d_i$, and U_{ij} is the Coulomb charging energy between electrons on dots i and j (in all calculations we include only nearest neighbor interactions). The source ($r = S$) and drain ($r = D$) electrodes are described by H_{res} , where $n_{pr} = c_{pr}^\dagger c_{pr}$ is the number operator for electrons in state p . The electrons in the electrodes are as usual for good metals modelled as being non-interacting. H_T^i describes tunneling between electrode $r = S, D$ and molecule i , which takes place with amplitude t_{ri} . We assume both the tunnel amplitude and the electrode densities of states, ρ_r , to be energy-independent. In this case, the tunnel rates, $\Gamma_{ri} = 2\pi\rho_r|t_{ri}|^2/\hbar$, which set the inverse time-scale for single-electron tunneling, are also energy-independent.

Transport through a homogeneous layer. We consider first a homogeneous monolayer, i.e., $U_{ij} = U$, $\Gamma_{ri} = \Gamma_r$, and $\epsilon_i = \epsilon$. We also focus on the regime where transport is dominated by single-electron tunneling, which is the case in the weak tunnel coupling regime, $\hbar\Gamma < k_B T$, where T is the temperature. We arbitrarily pick one molecule in the monolayer and denote it by M1. Our aim is now to calculate the stationary current flowing through the LUMO of M1. In the single-electron tunneling regime, the current is carried by processes in which a single electron tunnels either from one electrode into M1, or from M1 into one electrode, with rates proportional to the probability that M1 is empty, $P^{(0)}$, or full, $P^{(1)}$, respectively. However, because of U , the rates also depend on the occupation of the N nearest neighbors of M1, which we denote M2. We therefore consider probability distributions of the form $P_k^{(m)}$: The probability that M1 is empty ($m = 0$) or occupied ($m = 1$), while k of its neighbors are occupied. The net current from reservoir r into M1 is then

$$I_r = -e \sum_{k=0}^N \left(W_r^+(kU) P_k^{(0)} - W_r^-(kU) P_k^{(1)} \right), \quad (4)$$

where $W_r^\pm(E) = \Gamma_r f^\pm((E + \epsilon - \mu_r)/k_B T)$, $f^+(x)$ is the fermi function, $f^-(x) = 1 - f^+(x)$, and $\mu_r = \pm eV/2$

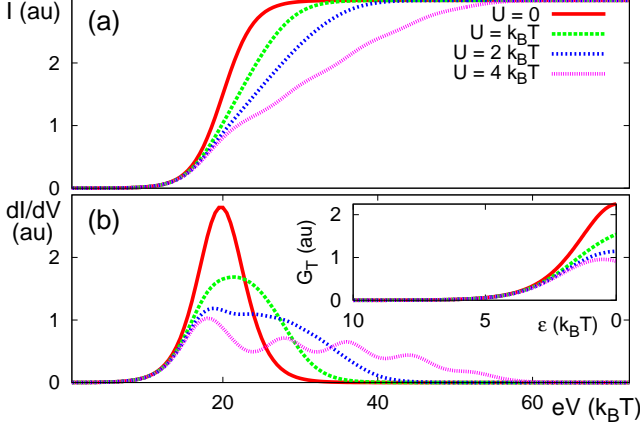


FIG. 2. (Color online). $I(V)$, (a), and $dI(V)/dV$, (b), for $\epsilon = 10k_B T$ and increasing strength of the inter-molecular Coulomb interaction, $U = 0, \dots, 4k_B T$. We have assumed a square lattice configuration, where each molecule has $N = 4$ nearest neighbors. I and dI/dV are given in arbitrary units (au) since $I \propto \Gamma$ in the single-electron tunneling regime. The inset in (b) shows the linear conductance, G_T , as a function of the position of the LUMO relative to the Fermi energy.

for $r = S/D$ is the chemical potential of electrode r . We assume that the bias drop occurs symmetrically at the two tunnel barriers, such that ϵ is independent of V . The total current is $I = N_M I_D = -N_M I_S$, where N_M is the total number of molecules in the monolayer.

The remaining problem is to find a master equation to determine $P_k^{(m)}$ under non-equilibrium conditions, i.e., to find the voltage-induced charging of the interacting monolayer. In the supplementary online information [22], we present the complete master equation and the full derivation, and also compare solutions within different approximation schemes. Here we merely mention that a master equation for $P_k^{(m)}$ involves tunneling into and out of both M1 (changing m) and M2 (changing k). The latter terms are proportional to the *conditional probabilities*, $P_{k,k'}^{(m,n)}$: The probability that M2 is occupied ($n = 1$) or empty ($n = 0$) and has k' occupied neighbors, *given that* M1 is occupied ($m = 1$) or empty ($m = 0$) with k occupied neighbors. The master equation for $P_{k,k'}^{(m,n)}$ in turn involves higher order conditional probabilities, $P_{k,k',k''}^{(m,n,l)}$. In the results presented here, we close the hierarchy of equations by neglecting explicit three-charge correlations (replacing $P_{k,k',k''}^{(m,n,l)} \rightarrow P_{k',k''}^{(n,l)}$). One is then left with solving a non-linear master equation for $P_{k,k'}^{(m,n)}$, which have to be inserted into the equation for $P_k^{(m)}$.

Figure 2 shows the results of the master equation calculations for $U = 0, \dots, 4k_B T$. When $U = 0$, $I(V)$ shows a thermally broadened step when the LUMO enters into the bias window, which acquires some additional broadening for $U \lesssim k_B T$. When $U > k_B T$, several current

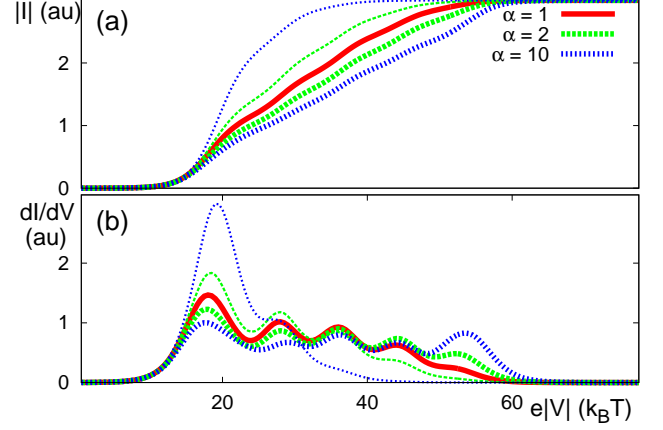


FIG. 3. (Color online). $|I|$, (a), and dI/dV , (b), as a function of V (thick lines) or $-V$ (thin lines), for $\epsilon = 10k_B T$, $U = 4k_B T$, and $N = 4$. We vary the ratio between the source and drain tunnel couplings, $\alpha = \Gamma_S/\Gamma_D$, while keeping $\bar{\Gamma} = \Gamma_S \Gamma_D / (\Gamma_S + \Gamma_D)$ fixed, which fixes the value of the current plateau at large V .

steps (multiple sidepeaks in dI/dV) can be discerned. They are separated in voltage by U and correspond to the condition that charging M1 becomes possible, also when $k = 1, 2, \dots, N$ of M2 are charged. There are only N satellite conductance peaks, since the maximum interaction cost of adding one electron is NU , and the peaks are always equidistant. This makes it possible to experimentally distinguish sidepeaks originating from inter-molecular Coulomb interaction from similar features related to higher lying orbitals or vibronic excitations. For all values of U , the current saturates at the same value, corresponding to a fully conducting monolayer. The inset of Fig. 2(b) shows the linear conductance as a function of the position of the LUMO relative to the electrode Fermi energy. Unless the LUMO is close to resonance, the charging of the monolayer is rather small and the inter-molecular Coulomb interactions are relatively unimportant.

Figure 3 shows $I(V)$ and $dI(V)/dV$ for a monolayer with a larger coupling to the source than the drain, $\Gamma_S > \Gamma_D$. For $U \neq 0$, this introduces an asymmetry into the current voltage characteristics, $I(V) \neq -I(-V)$. The reason is that there is now a larger charging of the monolayer for $V > 0$ compared with $V < 0$ since, for positive bias, electrons can easily tunnel into the monolayer (from the source), but cannot easily escape again (to the drain), while the situation is reversed for negative bias. A larger charging increases the effects of interactions and causes the $I(V)$ curve to become flatter and dI/dV to show more pronounced sidepeaks. For $U = 0$, asymmetric tunnel couplings do not introduce any asymmetry into the $I(V)$ curve. There are several other possible reasons for an asymmetric $I(V)$, but the rather special form seen

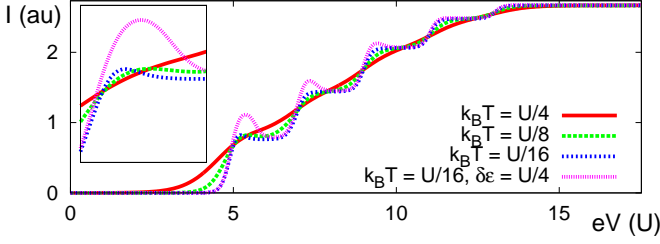


FIG. 4. (Color online). $I(V)$ for $\epsilon = 5U/2$, $N = 4$, and successively lowered T . One molecule (out of nine) has $\Gamma_D = \Gamma_S/100$. In the magenta curve, we have furthermore assumed the LUMO of the asymmetrically coupled molecule to be $\delta\epsilon = U/4$ higher in energy compared with the others. The inset zooms in on the first current step.

in Fig. 3 nonetheless provides a fingerprint of the intermolecular Coulomb interaction.

NDR in inhomogeneous layers. Finally, we investigate the effects of disorder within the molecular monolayer. Here, it is no longer possible to use our master equation approach, which assumes a homogeneous monolayer. Instead, we take a finite number of molecules, which may all have different properties, and diagonalize the corresponding many-body Hamiltonian exactly. The many-body eigenstates can then be used in a standard master equation approach [23] to calculate the current. Due to the rapidly growing size of the Hilbert space, only a rather small number of molecules can be included. However, as we show in the supplementary online information [22] for the case of a homogeneous monolayer, using 3×3 molecules and periodic boundary conditions gives excellent agreement with the infinite monolayer master equation.

Figure 4 shows the result of these calculations, where we have assumed one molecule (out of nine) to be only weakly coupled to the drain electrode, $\Gamma_D = \Gamma_S/100$. The asymmetrically tunnel coupled molecule now acts as a charge trap, since for $V > 2\epsilon$ it can be filled with an electron tunneling in from the source, which is then prevented from escaping to the drain. The intermolecular Coulomb interaction means that the occupation of the charge trap prevents transport through neighboring molecules, unless the bias voltage is increased further. As the temperature is reduced, this leads to a weak NDR at the first current plateau. A much stronger NDR effect, which is repeated on every current plateau, is obtained if the LUMO of the asymmetrically coupled molecule lies at a slightly higher energy compared with the other molecules (see magenta curve in Fig. 4). This is a realistic scenario since the asymmetrically coupled molecule experiences less screening from conduction electrons in the electrodes and, in general, a different chemical and electrostatic environment. The reason for the larger NDR is that, due to the misalignment, a large current is first allowed to flow through the symmetrically

coupled molecules, before the charge trap becomes filled at higher voltages. For the configuration in Fig. 4, with a molecule weakly coupled to the drain, the $I(V)$ curve will be asymmetric, with no NDR for negative bias. However, in a large monolayer, if approximately the same number of molecules are weakly coupled to the source and to the drain, the voltage symmetry is approximately restored with NDR for both bias polarities.

Conclusions. We have studied electric transport through a large number of mesoscopic conductors contacted in parallel, and shown that Coulomb interactions between charge carriers on neighboring conductors give rise to distinct features in the non-linear current-voltage characteristics. Our detailed calculations allow these interaction-induced features to be identified and isolated from the single-device properties, which is essential when using electric transport as a spectroscopic tool. Furthermore, we have shown that interactions can give rise to negative differential resistance if some of the conductors are significantly coupled to only one electrode. Our results may aid in the interpretation of past and future experiments, for example on molecular monolayer devices. There has been much recent interest in molecular thermoelectric devices [24, 25] because of the sharp nature of the transport resonances [26]. The results of our study, showing an effective interaction-induced broadening of the transport resonances, is likely to have a large impact on the thermoelectric efficiency. Finally, the general theoretical framework, derived in the supplementary information [22], should form a useful basis for future studies of transport through interacting mesoscopic conductors.

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SUPPLEMENTARY INFORMATION

General master equations

We start by deriving general expressions for the current through the interacting molecular monolayer, and its nonequilibrium charging, focusing on the single electron tunneling regime. We consider a homogeneous monolayer and (arbitrarily) pick one molecule (denoted M1). We want to calculate the steady-state current flowing from electrode r into M1, which is given by (see Eq. (4) in the main paper)

$$I_r = -e \sum_{k=0}^N \left(W_r^+(kU) P_k^{(0)} - W_r^-(kU) P_k^{(1)} \right), \quad (5)$$

where $P_k^{(m)}$ denotes the probability that M1 is empty ($m = 0$) or occupied ($m = 1$), while k of its neighbors are occupied. N is the number of nearest neighbor molecules, μ_r is the chemical potential of electrode r , U is the Coulomb repulsion between electrons occupying nearest neighbor molecules, and the rates are defined by $W_r^\pm(E) = \Gamma_r f^\pm((E + \epsilon - \mu_r)/k_B T_r)$, with $f^+(x)$ being the fermi function and $f^-(x) = 1 - f^+(x)$. ϵ is the energy of the single spinless molecular orbital we take into account and Γ_r is the tunnel coupling between M1 and electrode r . Since it has no impact on the structure of the general theory, we allow for different temperatures in the different electrodes, $T_r \neq T_{r'}$.

Because of the interactions, the current through M1 depends on the occupation of its neighbors, i.e., on the nonequilibrium charging of the monolayer. Thus, in order to calculate the current using Eq. (5), we have to determine the occupation probability distributions, $P_k^{(m)}$. To do so, we now derive a new type of master (or rate) equation. Just as in a normal master equation, the time derivative of an occupation probability is given by the sum of all tunnel processes enhancing that occupation, minus all tunnel processes decreasing that occupation, each process being weighted by the occupation probability of the corresponding initial state. We obtain

$$\begin{aligned} \dot{P}_k^{(1)} = & W^+(kU) P_k^{(0)} - W^-(kU) P_k^{(1)} \\ & - N \sum_{k'=1}^N \left[W^-(k'U) P_{k,k'}^{(1,1)} + W^+(k'U) P_{k,k'}^{(1,0)} \right] P_k^{(1)} \\ & + N \sum_{k'=1}^N \left[W^-(k'U) P_{k+1}^{(1)} P_{k+1,k'}^{(1,1)} \right. \\ & \left. + W^+(k'U) P_{k-1}^{(1)} P_{k-1,k'}^{(1,0)} \right], \end{aligned} \quad (6)$$

$$\begin{aligned}
\dot{P}_k^{(0)} = & -W^+(kU)P_k^{(0)} + W^-(kU)P_k^{(1)} \\
& - N \sum_{k'=0}^{N-1} \left[W^-(k'U)P_{k,k'}^{(0,1)} + W^+(k'U)P_{k,k'}^{(0,0)} \right] P_k^{(0)} \\
& + N \sum_{k'=0}^{N-1} \left[W^-(k'U)P_{k+1,k'}^{(0,1)} \right. \\
& \left. + W^+(k'U)P_{k-1,k'}^{(0,0)} \right], \tag{7}
\end{aligned}$$

where $W^\pm(E) = \sum_r W_r^\pm(E)$. The first line in Eqs. (6) and (7) is just like in a standard master equation, describing the increase (decrease) in occupation of M1 due to tunneling into (out of) it. The second (third and forth) lines describe the decrease (increase) in $P_k^{(m)}$ due to tunneling into or out of one of M2 (nearest neighbors of M1), which changes k . Here for example $P_{k,k'}^{(1,1)}$ denotes the *conditional* probability that an M2 is occupied and has k' occupied neighbors, *given that* M1 is occupied with k

occupied nearest neighbors. Note that k' runs from 1 to N in the equation for $P_k^{(1)}$, but from 0 to $N-1$ in the equation for $P_k^{(0)}$. The reason is that if M1 is occupied, M2 has to have at least one occupied nearest neighbor, and if M1 is unoccupied, M2 can at the most have $N-1$ occupied neighbors.

In the steady-state limit, which is assumed in all results presented here and in the main paper, we can set all time derivatives to zero in Eqs. (6) and (7), as well as in all master equations appearing below.

Equations (6) and (7) have to be supplemented with a condition expressing probability normalization:

$$\sum_k \left(P_k^{(0)} + P_k^{(1)} \right) = 1. \tag{8}$$

The average charge on M1 is given by $\langle q \rangle = -e \sum_k P_k^{(1)}$.

Clearly, we also have to find the quantities $P_{k,k'}^{(m,n)}$, which satisfy similar master equations

$$\begin{aligned}
\dot{P}_{k,k'}^{(1,1)} = & W^+(k'U)P_{k,k'}^{(1,0)} - W^-(k'U)P_{k,k'}^{(1,1)} \\
& - N_- \sum_{k''=1}^N \left[W^-(k''U)P_{k,k',k''}^{(1,1,1)} + W^+(k''U)P_{k,k',k''}^{(1,1,0)} \right] P_{k,k'}^{(1,1)} \\
& + N_- \sum_{k''=1}^N \left[W^-(k''U)P_{k,k'+1}^{(1,1)} P_{k,k'+1,k''}^{(1,1,1)} + W^+(k''U)P_{k,k'-1}^{(1,1)} P_{k,k'-1,k''}^{(1,1,0)} \right], \tag{9}
\end{aligned}$$

$$\begin{aligned}
\dot{P}_{k,k'}^{(0,0)} = & -W^+(k'U)P_{k,k'}^{(0,0)} + W^-(k'U)P_{k,k'}^{(0,1)} \\
& - N_- \sum_{k''=0}^{N-1} \left[W^-(k''U)P_{k,k',k''}^{(0,0,1)} + W^+(k''U)P_{k,k',k''}^{(0,0,0)} \right] P_{k,k'}^{(0,0)} \\
& + N_- \sum_{k''=0}^{N-1} \left[W^-(k''U)P_{k,k'+1}^{(0,0)} P_{k,k'+1,k''}^{(0,0,1)} + W^+(k''U)P_{k,k'-1}^{(0,0)} P_{k,k'-1,k''}^{(0,0,0)} \right], \tag{10}
\end{aligned}$$

$$\begin{aligned}
\dot{P}_{k,k'}^{(1,0)} = & -W^+(k'U)P_{k,k'}^{(1,0)} + W^-(k'U)P_{k,k'}^{(1,1)} \\
& - N_- \sum_{k''=0}^{N-1} \left[W^-(k''U)P_{k,k',k''}^{(1,0,1)} + W^+(k''U)P_{k,k',k''}^{(1,0,0)} \right] P_{k,k'}^{(1,0)} \\
& + N_- \sum_{k''=0}^{N-1} \left[W^-(k''U)P_{k,k'+1}^{(1,0)} P_{k,k'+1,k''}^{(1,0,1)} + W^+(k''U)P_{k,k'-1}^{(1,0)} P_{k,k'-1,k''}^{(1,0,0)} \right], \tag{11}
\end{aligned}$$

$$\begin{aligned}
\dot{P}_{k,k'}^{(0,1)} = & W^+(k'U)P_{k,k'}^{(0,0)} - W^-(k'U)P_{k,k'}^{(0,1)} \\
& - N_- \sum_{k''=1}^N \left[W^-(k''U)P_{k,k',k''}^{(0,1,1)} + W^+(k''U)P_{k,k',k''}^{(0,1,0)} \right] P_{k,k'}^{(0,1)} \\
& + N_- \sum_{k''=1}^N \left[W^-(k''U)P_{k,k'+1}^{(0,1)} P_{k,k'+1,k''}^{(0,1,1)} + W^+(k''U)P_{k,k'-1}^{(0,1)} P_{k,k'-1,k''}^{(0,1,0)} \right], \tag{12}
\end{aligned}$$

where $N_- = N-1$. $P_{k,k',k''}^{(1,1,l)}$, for example, denotes

the conditional probability that a next-nearest neighbor

molecule (M3) is occupied ($l = 1$) or empty ($l = 0$), with k'' occupied nearest neighbors, given that M1 is occupied with k occupied nearest neighbors and M2 is occupied with k' occupied nearest neighbors. Clearly, a master equation for $P_{k,k',k''}^{(m,n,l)}$ will involve even higher order conditional probabilities, expressing the fact that transport through the whole monolayer is in principle correlated. Below we will describe approximations which make the system of equations close.

Just as the normal occupation probabilities, the conditional probabilities must be normalized. This gives rise to the additional equations:

$$1 = \sum_{k'=0}^{N-1} \left(P_{k,k'}^{(0,0)} + P_{k,k'}^{(0,1)} \right), \quad (13)$$

$$1 = \sum_{k'=1}^N \left(P_{k,k'}^{(1,0)} + P_{k,k'}^{(1,1)} \right). \quad (14)$$

In addition, we have

$$0 = P_{k,N}^{(0,j)} = P_{k,0}^{(1,j)} = P_{N,k'}^{(i,0)} = P_{0,k'}^{(i,1)}, \quad (15)$$

since, for example, M2 must have at least one occupied neighbor if M1 is occupied.

There is a further possible simplification due to the homogeneous nature of the monolayer: Since all M2 molecules are equivalent, if M1 has k occupied neighbors, each M2 should be occupied with probability k/N . This gives the conditions

$$\frac{k}{N} = \sum_{k'=0}^N P_{k,k'}^{(m,1)}, \quad (16)$$

$$1 - \frac{k}{N} = \sum_{k'=0}^N P_{k,k'}^{(m,0)}. \quad (17)$$

When $P_{k,k'}^{(m,n)}$ fulfill Eqs. (16) and (17), they also automatically fulfill the standard normalization conditions, Eqs. (13) and (14). However, Eqs. (16) and (17) give twice as many conditions as Eqs. (13) and (14), and should be used instead of the first line in Eqs. (9)–(12), corresponding to the terms changing n in $P_{k,k'}^{(m,n)}$. Thus, the occupation of M2 should not be determined by the master equation, but is instead fixed by k . We therefore use the master equation only to solve for the k' -dependence of $P_{k,k'}^{(m,n)}$.

Mixed mean-field approximation

We start with a very simple approximation to close the system of master equations involving ever higher orders of conditional probabilities. This approximation is not used in any of the results in the main paper, but is included here since it provides a simple and intuitive method, which is valid for moderate values of the interaction strength, $U \lesssim k_B T$. We treat the interactions between M1 and M2 exactly, while the interactions between M2 and M3 are treated within a mean-field approximation. In the master equations for $P_k^{(m)}$, we should then replace $k'U$ by $N_- \langle n \rangle U$ in Eq. (7) (for $m = 0$) and by $(1 + N_- \langle n \rangle)U$ in Eq. (6) (for $m = 1$), where $\langle n \rangle$ is the average occupation of the $N + 1$ molecules M1 and M2, given by

$$\langle n \rangle = \frac{1}{N+1} \sum_{k'} \left[P_{k'}^{(1)} + N k' \left(P_{k'}^{(1)} + P_{k'}^{(0)} \right) \right]. \quad (18)$$

After this approximation, W^\pm in Eqs. (6) and (7) no longer depend on k' and we can use Eqs. (16) and (17) to carry out the sums over the conditional probabilities $P_{k,k'}^{(m,n)}$. Thus, we do not need to solve Eqs. (9)–(12), but can directly solve Eqs. (6) and (7), which have now become

$$\begin{aligned} \dot{P}_k^{(1)} &= W^+(kU)P_k^{(0)} - W^-(kU)P_k^{(1)} \\ &\quad - N \left\{ \frac{k}{N} W^- [(1 + N_- \langle n \rangle)U] + \left(1 - \frac{k}{N} \right) W^+ [(1 + N_- \langle n \rangle)U] \right\} P_k^{(1)} \\ &\quad + N \left\{ \frac{k+1}{N} W^- [(1 + N_- \langle n \rangle)U] P_{k+1}^{(1)} + \left(1 - \frac{k-1}{N} \right) W^+ [(1 + N_- \langle n \rangle)U] P_{k-1}^{(1)} \right\}, \end{aligned} \quad (19)$$

$$\begin{aligned} \dot{P}_k^{(0)} &= W^-(kU)P_k^{(1)} - W^+(kU)P_k^{(0)} \\ &\quad - N \left[\frac{k}{N} W^- (N_- \langle n \rangle U) + \left(1 - \frac{k}{N} \right) W^+ (N_- \langle n \rangle U) \right] P_k^{(0)} \\ &\quad + N \left[\frac{k+1}{N} W^- (\langle n \rangle N_- U) P_{k+1}^{(0)} + \left(1 - \frac{k-1}{N} \right) W^+ (N_- \langle n \rangle U) P_{k-1}^{(0)} \right]. \end{aligned} \quad (20)$$

Together with probability normalization, Eq. (8), this makes a closed set of equations, which, however, has to

be solved self-consistently together with Eq. (18) because

of the dependence on $\langle n \rangle$. The resulting occupations, $P_k^{(m)}$, can then be inserted into Eq. (5) to calculate the current.

Note that in Eqs. (19) and (20), and in Eq. (5) for the current, kU appears explicitly in the terms involving tunneling into and out of M1 and, in addition, the relevant interaction for tunneling into M2 is $(1 + N_- \langle n \rangle)U$ if M1 is occupied [Eq. (19)], but $N_- \langle n \rangle U$ if M1 is unoccupied [Eq. (19)]. This reflects the fact that the M1–M2 interactions are treated exactly. Therefore, these master equations are capable of producing steps in the nonequilibrium monolayer charging and current, for example as a function of increasing bias voltage V , and is applicable for $U \lesssim k_B T$, see Fig. 5. This is in contrast to the much simpler standard mean-field approximation, which would consist of simply solving only the first line in Eqs. (19) and (20), with $kU \rightarrow P^{(1)}U = \sum_k P_k^{(1)}U$, in which case the whole equation can be summed over k . The standard mean-field approach fails completely unless $U \ll k_B T$ (not shown in Fig. 5).

Also note that since we treat the M1 and M2 molecules within a different level of approximation, $\langle n \rangle \neq P^{(1)}$, although we numerically always find them to be compara-

ble, unless $U \gg k_B T$. Similarly, if we instead of using Eq. (5) to calculate the current, calculated the average current through M1 and M2, we would obtain a slightly different result.

Truncating the correlations

We now introduce the approximation scheme which is used for the calculations presented in Figs. 2 and 3 in the main paper, which does not rely on a mean-field treatment at any level and is applicable also in the regime $U > k_B T$. This is obtained by only taking conditional probabilities up to some given order explicitly into account. Here, we simply neglect explicit three-charge correlation terms when solving the set of master equations, which means that we replace $P_{k,k',k''}^{(m,n,l)} \rightarrow P_{k',k''}^{(n,l)}$ (note that since we are dealing with conditional probabilities, we should not factorize the expressions, i.e., we should *not* include a factor $P_k^{(m)}$ on the right hand side). Now the equations for the conditional probabilities, Eqs. (9)–(12), become

$$\begin{aligned} \dot{P}_{k,k'}^{(1,1)} = & -N_- \sum_{k''=1}^N \left[W^-(k''U) P_{k',k''}^{(1,1)} + W^+(k''U) P_{k',k''}^{(1,0)} \right] P_{k,k'}^{(1,1)} \\ & + N_- \sum_{k''=1}^N \left[W^-(k''U) P_{k,k'+1}^{(1,1)} P_{k'+1,k''}^{(1,1)} + W^+(k''U) P_{k,k'-1}^{(1,1)} P_{k'-1,k''}^{(1,0)} \right], \end{aligned} \quad (21)$$

$$\begin{aligned} \dot{P}_{k,k'}^{(0,0)} = & -N_- \sum_{k''=0}^{N-1} \left[W^-(k''U) P_{k',k''}^{(0,1)} + W^+(k''U) P_{k',k''}^{(0,0)} \right] P_{k,k'}^{(0,0)} \\ & + N_- \sum_{k''=0}^{N-1} \left[W^-(k''U) P_{k,k'+1}^{(0,0)} P_{k'+1,k''}^{(0,1)} + W^+(k''U) P_{k,k'-1}^{(0,0)} P_{k'-1,k''}^{(0,0)} \right], \end{aligned} \quad (22)$$

$$\begin{aligned} \dot{P}_{k,k'}^{(1,0)} = & -N_- \sum_{k''=0}^{N-1} \left[W^-(k''U) P_{k',k''}^{(0,1)} + W^+(k''U) P_{k',k''}^{(0,0)} \right] P_{k,k'}^{(1,0)} \\ & + N_- \sum_{k''=0}^{N-1} \left[W^-(k''U) P_{k,k'+1}^{(1,0)} P_{k'+1,k''}^{(0,1)} + W^+(k''U) P_{k,k'-1}^{(1,0)} P_{k'-1,k''}^{(0,0)} \right], \end{aligned} \quad (23)$$

$$\begin{aligned} \dot{P}_{k,k'}^{(0,1)} = & -N_- \sum_{k''=1}^N \left[W^-(k''U) P_{k',k''}^{(1,1)} + W^+(k''U) P_{k',k''}^{(1,0)} \right] P_{k,k'}^{(0,1)} \\ & + N_- \sum_{k''=1}^N \left[W^-(k''U) P_{k,k'+1}^{(0,1)} P_{k'+1,k''}^{(1,1)} + W^+(k''U) P_{k,k'-1}^{(0,1)} P_{k'-1,k''}^{(1,0)} \right]. \end{aligned} \quad (24)$$

Together with Eqs. (16) and (17), these equations can be solved for $P_{k,k'}^{(m,n)}$. The conditional probabilities are

then inserted into the master equations for the occupa-

tion probabilities, Eqs. (6) and (7), which can be solved for $P_k^{(m)}$, from which we then calculate the current using Eq. (5).

One complication is that Eqs. (21)–(24) are non-linear, involving terms like $P_{k,k'}^{(m,n)} P_{k',k''}^{(n,l)}$. Numerically we can deal with this simply by picking some initial distribution for the conditional probabilities which originate from the truncated higher order terms ($P_{k',k''}^{(n,l)}$), and then solve the equations iteratively, updating this distribution each time. Note that what remains are only equations for each distribution as a function of k' , i.e., we only need to solve for the k' -dependence of $P_{k,k'}^{(m,n)}$. Thus, we only ever have to solve equations of size $N \times N$, although there are $4 \times N$ such equations (one for each m , n , and k) which all have to be solved within each iteration. As demonstrated in Fig. 5, the results are reliable for much larger values of $U/k_B T$ compared with the mixed mean-field approximation introduced above.

Exact diagonalization of a finite monolayer

The master equation method described above is suitable only for an infinite homogeneous monolayer. To study an inhomogeneous monolayer, e.g., involving defect sites, we rely instead on a standard master equation solution for a finite monolayer. We take a finite number of molecules (3×3 molecules on a quadratic lattice is used in all results) and diagonalize exactly the corresponding monolayer Hamiltonian, $\sum_i H_{\text{ML}}^i$ in Eq. (1) in the main paper. Since the total charge in the monolayer, N_C , commutes with $\sum_i H_{\text{ML}}^i$, we can label the many-body eigenstates with N_C , and, since we do not consider inter-molecular tunneling, each eigenstate can be chosen to correspond to a given distribution of these charges over the different molecules. We thus label the eigenstates $|aN_C\rangle$, where a labels the charge configuration. The master equation is now solved for the occupation probabilities, p_{aN_C} , of these eigenstates, which can then be used to calculate the steady-state current from electrode r into the monolayer

$$\dot{p}_{aN_C} = \sum_{s=\pm 1} \sum_{a'} \left(K_{aN_C, a'(N_C+s)}^s p_{a'(N_C+s)} - K_{a'(N_C+s), aN_C}^{-s} p_{aN_C} \right), \quad (25)$$

$$1 = \sum_{aN_C} p_{aN_C}, \quad (26)$$

$$I_r = -e \sum_{aN_C} \sum_{s=\pm 1} \sum_{a'} s K_{a'(N_C+s), aN_C}^{r,s} p_{aN_C}, \quad (27)$$

where the rate matrix is given by

$$K_{aN_C, a'(N_C+s)}^{r,s} = \Gamma_{aN_C, a'(N_C+s)} \times f^s \left[(E_{a'(N_C+s)} - E_{aN_C} - \mu_r) / k_B T_r \right], \quad (28)$$

and $K_{aN_C, a'(N_C+s)}^s = \sum_r K_{aN_C, a'(N_C+s)}^{r,s}$. Since we do not assume a homogeneous monolayer, the tunnel rates, $\Gamma_{aN_C, a'(N_C+s)}$, depend on both the initial and final many-body eigenstates. In particular, $\Gamma_{aN_C, a'(N_C+s)} = 0$ whenever $|aN_C\rangle$ and $|a'(N_C+s)\rangle$ do not simply differ by the occupation of a single molecule, since this is all that can be changed by a single SET process.

Equation (25) simply expresses the fact that the change in occupation of state $|aN_C\rangle$ is determined by the sum of all tunnel processes filling $|aN_C\rangle$, weighted by the occupations of the corresponding initial states, minus all tunnel processes emptying $|aN_C\rangle$. In the steady state limit, the left hand side of Eq. (25) is set to zero. Probability normalization is enforced by Eq. (26). The current from electrode r , Eq. (27), is given by the sum of all processes involving an electron tunneling into the monolayer from electrode r , minus the sum of all processes where an electron tunnels out of the monolayer into electrode r , weighted by the corresponding occupation probabilities.

The method described here is used in the final part of the main paper to investigate transport in an inhomogeneous molecular monolayer, where some molecules couple only weakly to one of the electrodes (and possibly also have a different LUMO energy). In Fig. 5, we use it instead to calculate transport through a homogeneous monolayer, allowing comparison with the infinite monolayer methods described above.

Comparison of different approximations

In Fig. 5, we compare the result of the different methods discussed above for different strengths of the inter-molecular Coulomb interaction, U . For $U = 0$ (not shown), all methods give completely identical results. Over the whole range of interaction strengths, we find excellent agreement between the results obtained by truncating the correlation, and those from the exact diagonalization of a finite monolayer. These are the approximation schemes used in the main paper. For $U \gg k_B T$, the mixed mean-field solution is clearly inaccurate, predicting the correct height of the high-voltage current plateau, as well as the correct position of the current steps, but failing to capture their height, and even erroneously predicting NDR for $U = 6k_B T$. Note that this method is not used in any of the results in the main paper.

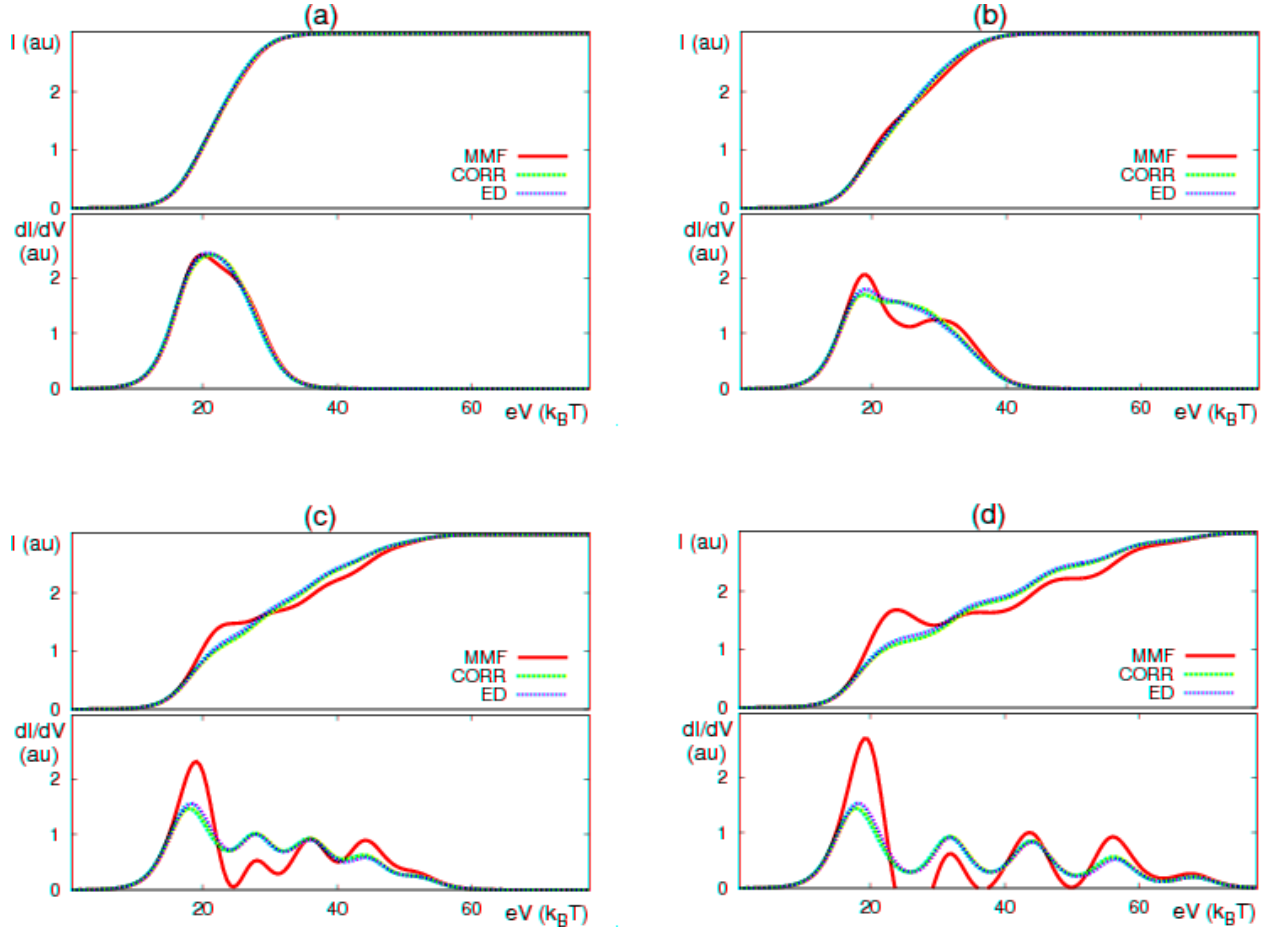


FIG. 5. Current (upper panel) and differential conductance (lower panel) as a function of applied bias voltage. In each subfigure, results using the three different methods described above are shown: Mixed mean-field approximation (MMF), truncation of correlations (CORR) and exact diagonalization of a finite monolayer (ED). We have everywhere used $\epsilon = 10k_B T$ and $N = 4$ (square lattice). In ED, we used a square lattice with 3×3 molecules, all with the same properties, and periodic boundary conditions [using instead open boundary conditions (not shown) does not qualitatively alter the results, but merely leads to a small increase in the height of the first peak and reduced height of the satellite peaks, reflecting the fact that interactions are somewhat less important in this case]. The strength of the inter-molecular Coulomb interaction is increased, with $U = k_B T$ in (a), $U = 2k_B T$ in (b), $U = 4k_B T$ in (c), and $U = 6k_B T$ in (d).